PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Process for the production of Coated Substrates

We, DEUTSCHE GOLD-UND SILBER-SCHEIDEANSTALT VORMALS ROESSIER, of 9, SILBERlaws of Germany, do hereby declare the invengranted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

The invention relates to a process for the. flat and web-like supports provided with antistatic to electrically conductive synthetic

plastic coatings or layers.

A considerable number of processes are already known for the production of coatings and coverings on many different types of supports, an example of such a process is lacquering in which resins and/or high-polymer substances are applied from solutions to a support and then dried to form a film. However, it is only possible in this way to form relatively thin layers. Aqueous dispersions of lacquers and/or synthetic plastics are also frequently used for similar coatings. This procedure is of very little use for the production of relatively thick coatings and is mainly used for impregnating textiles, for paints or for coatings on cardboard, paper and similar materials. Usually the use of such dispersions necessitates relatively long drying periods, sometimes even at stoving temperatures, so that a coherent film is formed. For the production of heavy coatings, as for example in the production of artificial leather, this process is not technically advantageous; on the contrary, synthetic plastic plastisols or synthetic plastic organosols are much more suitable for this purpose. By "plastisols," there is understood in this connection a mixture of a finely divided synthetic plastic in powder form (e.g. polyvinyl-chloride and/or vinyl-chloride copolymers) with suitable plasticisers, whereas dissipated or where for any other reasons "organosols" contain more or less large quan-conductive but also to a certain degree elastic

tities of volatile organic solvents as well as these constituents. These compositions are Weissfrauenstrasse, Frankfurt (Main), Ger-applied by brushing, casting, dipping or other many, a body corporate organised under the aknown methods of application to the supports to be coated and the coated supports are tion, for which we pray that a patent may be thereafter finally heated at relatively high temperatures. In this way, the solvent which may be present is driven off and the mixture of synthetic plastic and plasticiser gells. A dense coating is obtained which is more or less solid production of knitted and woven fabrics, and/or flexible and adheres to the support, fleeces, foils and like textile or non-textile which layer can be increased in thickness by repeated application and can, if desired, be provided with a final coating of a different composition.

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In addition to the constituents already mentioned, the coating compositions generally contain fillers, colouring agents, stabilisers and other known additives. Carbon black has been frequently recommended as a colouring agent for black layers. Quantities of 0.1 to 2%, depending on the nature of the carbon black, produce a very dark colour. In addition to the colouring effect the use of carbon black provides a degree protection against ageing of the synthetic plastic layer, for example due to weather influences. The quantities of carbon black necessary for the colouring can be incorporated without particular difficulties

into such coating pastes.

It is known in the rubber industry, in which substantially larger quantities of carbon black are used for the production of particular effects concerning the mechanical properties of the mixtures that it is possible, using special carbon blacks and, in some cases with observation of special precautions during manufacture, to obtain antistatic or electrically conductive mixtures. Such mixtures are particularly desirable and of importance in those cases where electrostatic charging must be avoided, where any static charging which may be present is to be

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constructional components are required.

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Since products produced from such rubber mixtures are not satisfactory for many purposes the need has long existed for the production of antistatic or electrically conductive charges on the local lands are the charges of the local lands are the local lands are the local lands are the lands are production of antistatic or electrically con perties, do not provide pastes which can be ductive coatings on all kinds of different brushed on the coatings. supports. However, all the synthetic plastics and plastic mixtures previously referred to del. and normally used for coating purposes have a quite high specific resistance and a tendency to electrostatic charging. This is for example shown with many plastics by the usually undesirable property of attracting and retaining particles of dust.

With these materials, the transmission and surface resistances are in the orders of magnitude of above 1011 ohm per cm, as also in the following, in accordance with the "principles for the electrical testing of insulating materials in accordance with VDE Specification 0303, Part 3). Consequently, quantities of electricity applied by friction of static charging cannot flow away and very high locally limited with resources become high, locally limited peak voltages become 25 possible in extreme cases, it can result in spark formation and consequently such synthetic plastics must not be used in zones where there is a danger of explosion, such as in underground mining.

large quantities of carbon black into rubber mixtures does not present any difficulties, because the introduction can be effected on the roller, it has hitherto not been possible for the quantities of carbon black necessary to produce anti-static or conductive layers to be incorporated into brushable coating pastes. The reason for this is that the follow-

passes, the reason for this is that the following three conditions must be simultaneously

40 satisfied for economic use:

1) The coating composition must be of suitable viscosity and suitable rheological behaviour, brushable, i.e. flexible and not liable to break, and also sufficiently stable and storable.

2) The coating produced was hardless.

carbon black for obtaining the required electrical properties could not be incorporated into brushable compositions which supply coatings or adequate mechanical strength; on the contrary, in order to produce the brushability, such a large quantity of plasticiser would have to be added to compositions with a corresponding carbon black content that the would have to be added to compositions with and gelled by the action of near.

The polyvinyl halides which can be used mechanical properties of the mixtures after with great advantage according to the invention include primarily polyvinyl chloride pro-

adequate and the coatings would be tacky on the surface; recipes with a high carbon black content, from which could be produced 'coatings' suitable as regards mechanical pro-

Attempts "have" been made to overcome these difficulties by using organosols. However, such compositions show inadequate rheological behaviour, are not stable in storage and become demixed or separated into components after a short time. Furthermore, it is only with very great difficulty that they can be processed to give thin layers, so that it is only possible by this process, as is known, to produce a kind of lacquer coating with coating quantities up to 30 g. per square metre.

As already described, only the pasting method is suitable for the production of relatively thick coatings and it has also already been mentioned that attempts have been made to incorporate suitable quantities of carbon black into such pastes by introduction of the carbon black in admixture with plasticisers. However, this has only been successful to a limited extent and only with organosols with the disadvantages described above.

It has now surprisingly been found that Whereas the incorporation of relatively the difficulties set forth here are overcome and layers obtained which are anti-static or conductive, depending on the carbon black concentration, by applying to the substrate a dispersion containing plastics into which has been incorporated electrically conductive 100 carbon black which has been converted with the aid of a wetting agent into a dispersion, and the coating is dried and set in known

In particular sheet like structures such as 105 woven and knitted fabrics, fleeces and foils can be provided with anti-static to electrically conducting synthetic plastic coating by the pasting method using mixtures of

a) polyvinylhalides and/or copolymers con- 110

and storable and s weight of carbon black is present, based on the weight of the vinyl compound, is incorporated into the plastisols for corganosols, which are known per se, this mixture is then applied to one or both sides of the support, 125 perhaps in several working steps, and dried and gelled by the action of heat.

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warms of their equipments the transferous sections on a company baselinarism of each or transferous section 1,015,353 december of many many transfer of the company of the anto an of these polymers with other copolymerisable fully when carrying out the process according to the invention. The substances available for the copolymerisation are in this case not, tion. These substances include particularly 15 acetate, vinyl alcohol, vinyl ether, vinyl chloracetal, vinyl thioether and vinyl acetylene, as and methacrylic acids and their esters, vinyl-20: idene chloride and vinylidene fluoride, sty-25 polymers and copolymers to the said vinyl halide polymers, provided that the presence thereof, as can easily be established, does not influence or does not substantially reduce the desired effect to be produced according to

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desired effect to be produced according to speed mixer mechanism, for example of the the invention.

For the production of the organosols, the "Ultra-Turrax" the words "Ultra-Turrax" usual organic solvents are added according are a Registered Trade Mark). to the invention, more especially those which "The suitable anion-active wetting agents are able to dissolve the polymers being used, include inter alia condensation products of 30 the invention.

For the production of the organosols, the to the invention, more especially those which are able to dissolve the polymers being used, 35 such as tetrahydrofuran, cyclohexanone,

methyl ethyl ketone and acetone. As a suitable plastisol it is possible to use

a conventional mixture of for example 50 to 70 parts by weight of polyvinyl halide to 50 and/orn advantageously; adhesion promoters. Polyvinyl chloride of various types obtained by emulsion polymerisation and having a K polyvinyl chloride suspensions and also additions of relatively small quantities of vinyl 50 chloride-vinyl clacetate copolymers, the K values of which can be between 45 and 65. the invention comprise particularly esters of 55 carbon atoms advantageously and phthalic acid; sebacic acid, azelaic acid and adipic acid, and also possibly polymers, such as polypropylene glycol adipate and/or so-called secondir ary plasticisers or extenders, such as hydro-60 carbon compounds, chlorinated hydrocarbons and derivatives of higher fatty alcohols.

As fillers, there, are to be considered known fillers, such as chalk, kaolin, talcum, alkaline earth carbonates or oxides, antimony tri-oxides, finely divided silicon or aluminium

duced by emulsion or suspension polymerisal axides, which are precipitated or obtained in tion and also, polyvinyl fluoride and polyvinyl; the gas phase. As stabilisers, there are pre-bromide. Copolymers, of monomers, forming, ferably used organic tin compounds or barium. cadmium compounds and, as adhesion promoters, isocyanates and/or polyurethanes, and epoxy compounds.

It has further been found to be advantage-

ous that the carbon black dispersion to be used in preponderant quantities and only in added to the plastisol or the organosol should quantities such that they have no disturbing consist of 10 to 30% by weight and preference on the process according to the invention. These substances include particularly having good electrical conductivity, about 2%. vinyl esters, such as vinyl acetate, vinyl pro- by weight of a wetting agent and the re-pionate, vinyl bromorropionate, vinyl chlor- mainder, of water. Such dispersions are low viscosity fluids and are stable for a long time acetal, vinyl thioether and vinyl acetylene, as because of the very fine dispersion of the well as other monomers available for copoly- carbon black. Sulphonic acid-formaldehyde merisation with vinyl halides, such as acrylic condensation products are advantageously used as wetting agents; however, it is also possible to use other anion-active substances, and also renes, acrylonitrile, butadiene, isoprene, with advantage non-ionic products, such as chloroprene, isobutylene, ethylene, propylene, addition products of ethylene oxide and commalcic and fumaric acid esters. It ies obviously pounds with reactive hydrogen. The production possible to add minor amounts of other known tion of such a dispersion is best effected by first of all making the carbon black into a thick paste in the solution of wetting agents and water and then producing a liquid carbon black dispersion with the aid of a high-speed mixer mechanism, for example of the

naphthalene-\$\beta\sulphonic acid and formalde-hyde, while the suitable non-ionic wetting agents include exethylation products of alkyl a conventional mixture of for example 50 to 70 parts by weight of polyvinyl halide to 50 to 30 parts by weight of plasticiser with suitable additions of fillers and/or stabilisers. Polyvinyl chloride of various types obtained by emulsion polymerisation and having a K value between 65 and 80 is advantageously to the suitable to consider mixtures of polyvinyl chloride suspensions and also addicorporated into the paste and the content of carbon black with good electrical conductivity in such dispersion should be so chosen according to the invention that the proportion of the carbon black in the synthetic plastic coating is at least 5%; based on the plastic content in the coating composition, but is advantaged by the plastic content in the coating composition, but is advantaged by the plastic content in the coating composition, but is advantaged by the plastic content in the coating composition, but is advantaged by the plastic content in the coating composition, but is advantaged by the plastic content in the coating composition, but is advantaged by the plastic content in the coating composition and the coating content in the coating co tageously even higher in order to guarantee the required properties of the final product; in order to obtain products which conduct electricity, it is advantageous to incorporate into the coating composition a proportion of carbon black which is higher than about 10%, once again based on the proportion of plastic. However, antistatic products are obtained with a content of about 5% of a so-called highly conductive carbon black. It will be readily understood that it is not possible to draw any sharp separation line between antistatic pro- 130

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perties and electrical conductivity of the synand said afthe types of carbon, black and with increasing are not too high, such as squeetimes occur in the synthetic plastic mixture, it is possible to produce a continuous rise in the electrical conductivity of the plastic coatings. It is surprising that the use of the aqueous carbon black dispersion permits the proportion of 10 carbon black to be increased to such an extent that surface resistances of about 10° ohms can be achieved, which can be considered as a very good result and completely adequate for the proposed purposes of use.

. According to the invention, types of carbon black which are already known as being highly conductive are used. These are found among the acetylene, furnace and channel carbon blacks; they are particularly distinguished by the common property that their specific surface area is greater than 100 m²/g. Such 6 10 de carbon blacks have very good electrical conductivity and also impart this property, to the " " atter products containing them; such as products MAN 250 Consisting of rubber. Types of carbon black with a lower specific surface, such as those which can be obtained by the processes rethe state ferred to; are likewise very good for conducting electric current. However, because of the different surface properties, they cannot be incorporated with equally good results into the starting mixtures which can be used according to the invention, because the conductivity of the articles produced from these mixtures when using such carbon blacks falls considerably as compared with those having types of carbon black recommended according to the invention and a substantially larger proportion of carbon black would have to be used in order to produce the required properties of the end products.

A carbon black which has proved particularly desirable in tests is one with a specific electrical resistance of 0.06 ohm x cm (measured at 300 atm.) with a mean particle size (arithmetic mean) of 277 A) and a surface tics; papers; cardboards or felts are also according to BET of 133 m²/g (Russ Corax suitable, as well as sheets of different metals. L of Degussa). However, corresponding active in Suitable stabilisers and adhesion promoters types of carbon black with even greater speci- amay be added where appropriate. 50 fic surfaces, such as 694 or 1030 m²/g (Russ sho The invention is further illustrated by the 115 activates A 26 and A 31 of Degussa) and a following Examples. other comparable carbon blacks; can also be satisfactorily used on a achievação

A particularly expedient method of incorporation of the carbon black is for the carbon. black dispersion to be slowly and gradually with low shearing stress for example with a normal propeller-type stirrer in quantities of up to 1:1 into the plastisol or the organosol to which may have been added additives which limit the pot life, such as special adhesion promoters and/or wetting agents. special polydiisocyanates, dimethacrylates, acrylates, polyesters are examples such additives. It is of great importance

that the shearing forces which become effective thetic plastic coatings. By suitable-choice of when the carbon black is being incorporated quantity of the proportion of carbon black in turbo mixers, and fluid mixers. It has in fact been found that the conductivity of the coatings obtained falls again if the compositions 'are worked too intensively.

If these manufacturing procedures are complied with, coatings compositions of excellent consistency, great stability and good workability are obtained. They are completely homogeneous, pliable and have the necessary viscosity; they have the necessary stability in storage and also do not separate before the doctor blade. This behaviour does not in any way conform to expectations, especially as the great difficulties already referred to have been found with the incorporation of carbon black into brushing compositions. It must therefore be considered as very surprising that the precess according to the invention leads, to products having the required electrical properties.

The pastes can be further processed by all conventional coating methods, for example by dipping, casting or by the various brushing methods. The coatings obtained after the final heating show very good mechanical strength values. The specific resistance of the coatings can be varied in any desired manner within the technically interesting limits of 10 -10⁴ olmis per cm. by the alteration of the quantities and type of carbon black without observing any important disadvantageous alteration in the mechanical properties of the 100 coatings or in the workability of the pastes.

As support for the coatings, it is possible with particular advantage to use woven or knitted fabrics or fleeces, the thread position of which can be more or less closed or open, and which consists of natural or synthetic fibres or yarns; artificial fibres of polyesters being particularly preferred with more open fabrics because of its mechanical strength. However, non-porous foils of synthetic plas- 110

Example 1.

20 parts by weight of an electrically highly conductive carbon black are formed into a paste with 2 parts by weight of a sulphonic 120 acidformaldehyde condensation product as wetting agent and 78 parts by weight of tap water and worked by means of a high-speed stirrer into a carbon black dispersion,

The carbon black dispersion is added to a 125 plastic dispersion which contains about 40% by weight of a vinyl chloride copolymer and also a plasticiser. By simple stirring, the carbon black is distributed in a completely uniform manner in the plastic dispersion. As 130

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will be seen from the following Table; the thanged even after the carbon black has been viscosity of the plastic dispersion remaind uned incorporated chyestirring: attracted to a traction of the plastic dispersion remaind uned incorporated chyestirring: attracted to a traction of the dispersion of

| Carbon black, addition in % by weight, calculated on plastic solid substance | Viscosity in Ford seconds 4 mm. nozzle immed— after after 5 hours 24 hours |
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The second dispersion of the second of the s (The establishment of the viscosity in Ford : . C. in another case. After drying, conductive seconds is known. The liquid to be measured ensilver electrodes were applied and the speis introduced into a standard beaker and a cific surface resistance determined with a it is allowed to run out through a nozzle spring tongue electrode with a length of 100 10 disposed in the bottom thereof. The running ... mm. and a spacing of 10 mm. out time in each case gives the viscosity in 10° (The measuring voltage was 4.5 volts up to Ford seconds). Paper board was coated with the mixed dis-didirect current. In other respects, the procedure persions prepared in this way and the material maccording to VDE 0303 δ 7 was used and the 15 was then subjected for 15 minutes to a tem- following measurement results were obtained: perature of 110° C: in one case and 170° in our 1 , rough the months as

Carbon black addition in % by weight. Viscosity in Ford seconds 4 mm. nozzle immed after after 24 hours 120 after calculated on plastic solid substance q in an a company of the part 12 12 1 152 mi 72 in me 18 due 12 - - aut 127 13 10 is 10 is

30 conductive carbon black are formed into a mountant of 40 parts by weight. In a manner paste as in Example 1 with 2 parts by weight analogous to Example 1, the viscosity was of a sulphonic acid-formaldehyde conflensa-in measured as a function of time. As is shown tion product as melting agent and 78 parts, from the values, indicated, the workability was by weight of tap water and mixed with a not made difficult in any way due to the 35 high-speed stirrer to form a carbon black disparticular method of, introducing carbon black

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1.7 C (1) 1 C of another suffer 20 parts by weight of a carbon black dispersion were added to 100 parts by weight of a basic composition, consisting of: 42.5% by weight of an emulsion polyvinyl chloride with the K value 75 which can be made into a paste, 33.5% by weight of dioctyl phthalate, 12.0% by weight of dioctyl adipate, 6.0% by weight of antimony trioxide, 10 1.0% by weight of barium-cadmium ·laurate. 5.0% by weight of polydiisocyanate (reaction product of toluylene - 2,4 - diisocyanate and a trihydric, aliphatic 15 alcohol). The carbon black dispersion consists of 22.5 parts by weight of a highly active furnace black (ash content 0.07%, BET surface 133, mean particle size 277 Å, vibrated weight 240 g/l, vibrated volume 420 cc/100 g., specific electrical resistance at 300 atm., 0.06 ohm per cm), 4 parts by weight of a nonionic wetting agent, such as the oxethylation products of aromatic oxy compounds, for example a condensation product of ethylene oxide and nonyl phenol, and 73.5 parts by weight of water. The admixing of the carbon black dispersion is effected slowly and in portions with the aid of a low-speed blade-type stirrer. Using a rubberised cloth coating machine, a nylon fabric with the thread position 9/9 35; the coating composition produced in this way,

consisting of 840 denier fibres is coated with the coating composition being applied as three coat-ings on each side, the layers having a total weight of about 270 g/m² on each side. After the coating operation, the web of material is conducted through a pre-heating channel, in which the heating is so adjusted that the web of material is not exposed to a temperature higher than about 100°. G. until the water content of the coating is completely evaporated. In a later section of the heating channel, the temperature is then raised to about 170° C., so that the coating gels out. By means of this process, there is formed a flexible, abrasion-resistant coated material which has a surface resistance of 2×10^6 to 2×10^7 ohms. This surface resistance was mea-

sured with the Siemens rod electrode in accordance with the VDE Specification 0303 referred to above. Coatings with the same basic composition but without addition of the carbon black dispersion have a surface resistance higher than 1010 ohms. EXAMPLE 4.
50 parts by weight of the carbon

black dispersion described in Example 1 are slowly added by means of a low-speed blade-type stirrer to 100 parts by weight of the basic composition also described according to Example 1. Using the coating composition as produced, which has

good spreading properties, a cotton fabric (thread position 23/22 consisting of yarns of the No. 34/34) and coated with a normal polyvinyl coloride priming coat (about 90 g/m²) is provided with additional coatings on one side on a rubberised cloth coating machine. In two operations, about 100 g/m² are applied and the material is further treated as described in Example 1.

The finished material has a surface resistance of about 1 x 104 ohms, measured with the Siemens rod electrode in accordance with the aforementioned VDE Specification 0303. The material is very flexible, dry to the touch

and resistant to abrasion. The efficacy of the process employed is clearly apparent from the foregoing Examples. The surface resistance can be lowered from the order of magnitude 10^9 to $10^1 \Omega$ by using the process according to the invention. This means that for the reliable production of an antistatic surface coating, a content of 8 to 10% by weight of carbon black must be produced in the plastic layer, while 25 to 30% by weight of carbon black must be incorporated into the plastic layers in order to have "good-conductivity" plastic coatings.

It is not possible for such quantities of

carbon black to be arranged in the plastic dispersions by direct addition, since in this case, as already described above, the plastic dispersions flocculate out and the films obtained are not flat, but are permeated with thick nodules of carbon black. Whe the process according to the invention is used, on the 100 contrary, completely smooth and lustrous films are produced at the low carbon black concentrations and completely smooth films with a slightly matt appearance with the high carbon black concentrations. The bonding strength is still satisfactory, even with relatively high carban black concentrations. Thickening agents for the production of brushing pastes can be added in the usual way. One particular advantage is also to he seen in the easy work- 110 ability which is produced when using the process according to the invention.
WHAT WE CLAIM IS:-

1. A process for the production of synthetic plastic layers or coatings on substrates by 115 applying a dispersion which contains plastics, wherein electrically conductive carbon black is converted with the aid of a wetting agent into a dispersion, the carbon black dispersion is combined with an aqueous dispersion of a 120 synthetic plastics material known per se, the carbon black-plastics dispersion is applied to the support and then is dried and fixed in known manner, the carbon being present in an amount of at least 51% by weight, based 125 on the weight of the plastics material.

2- A process as claimed in claim 1 wherein the coating is produced by the pasting method using a mixture of:

a) polyvinyl halides and/or copolymers 130

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with predominant proportions of vinyl halide; and advantageously 18 to 25% by weight of 25 b) plasticisers. an electrically conductive carbon black, about c) fillers, stabilisers and other known addi-2% by weight of a wetting agent and the re-FO IA CTIMEL OF THE PERIOD TWEST and if desired, O lattimetric to the lind if desired, imainder consists of water and of claims 1 wherein an electrically conductive carbon black to 4, wherein the carbon black dispersion in the form of an aqueous dispersion containing consists of 10 to 30% by weight of an eleca wetting agent is introduced into the plastitrically highly conductive carbon black, 2% 1 64. is sols or organosols known per se in a proporaby weight of an anion-active wetting agent, the 10 tion such that at least 5% by weight of the remainder being water. carbon black is present based on the weight of the vinyl compound, this mixture is then 7. A process as claimed in any of claims 1 to 6, wherein the carbon black dispersion applied on one or both sides to the support is incorporated into the plastisol or organosol possibly in several working steps, and is dried slowly and with low shearing stress in quan-15 and gelled by the action of hear. tities up to 1:1. 3. A process as claimed in claims 1 or 2 · 8. Coated substrates produced by the pro-wherein the substrate is a woven or knitted cess claimed in claim 1 substantially as defabric, a fleece or a foil. ethas allowers, with scribed with reference to any of the Examples. 4. A process as claimed in claim 1 wherein ELKINGTON & FIFE 20 the proportion carbon black in the coating is from 5 to 30%. Chartered Patent Agents 5. Process as claimed in any of claims 1 Bank Chambers, 329, High Holborn, to 4 wherein the aqueous carbon black dis--- London, W.G.1. persion consists of 10 to 30% by weight Agents for the Applicants. Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1965. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained. s to a linear or one of the later of the properties of the control of the decay function will be a second or one of the party. top may no हों। विकास क्षेत्रक अधिकार के स्वास के किस के किस है। किस किया के किस के किस के किस के किस के किस के किस के कि property and applicable of a state of the st get gent i tra promi et tald i more kwe i ak ne kombiken no eigent et nomeret i trakt The length of the general effekt trakt violet opphibliga kwe ja trock by (1) beneral i Committee of the commit te ale nativas as as autiliture serva saucest centitar menta. Hats processor en and a leaser and with a distance the metallic and and the filter of the entire a linguistic of shower and health the state that the state of the paper Standard Control of the American Michael Control of the Control of en all contents to be a content and content and content and man, and neglect a man and a man and a content a content and a content and a content and a content and a conte a shart we meaning the standards reminded of the lobustrigation uper of thems of teletral considers. The consideration and detailed a value of them 8 to training and the consideration of the consider complete and it cholest present one interest aborate that are working 18 and these one or piles of the states and an attendance of the states and an appearance of the analysis and A taken a notice of the control of t Within 20 courties for a thin wholey for the appropriate manner protein face or action of a fixed propriate programmer of changing and a manner of changing and changing of changing and changing of changing of the changing Parish or the district of the parish of the control of the parish of the control of the parish of th A State of Contract of Or HOME WINE START THE

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